(25)

19910107 98

COMPUTATIONAL MATERIALS SCIENCE AN EXAMPLE: NUMERICAL MODELING OF CHEMICAL VAPOR DEPOSITION PROCESSING OF ADVANCED FIBERS

Arnon Chait, Suleyman Gokoglu, and Maria Kuczmarski
NASA Lewis Research Center
Cleveland, Ohio

Pang Tsui
Sverdrup Technology, Inc.
Lewis Research Center Group
Brook Park, Ohio

Lisa Veitch
NASA Lewis Research Center
Cleveland, Ohio

David Thompson* and Ronald Gaug*
The University of Akron
Akron, Ohio

Computational materials science is a rapidly emerging discipline combining aspects from chemistry, fluid dynamics, and materials and computational sciences. This paper will detail the initial efforts undertaken in the Materials Division at Lewis to establish a dedicated facility for numerical and analytical simulations of materials processing. Computational Materials Laboratory activities are currently aimed at understanding and optimizing processes involving transport of heat, fluid, and mass. An ongoing combined experimental and numerical study is presented. It illustrates the growth of advanced fibers for high-temperature composite applications by using the chemical vapor deposition process. A comprehensive analysis of the three-dimensional heat and fluid flow inside the reactor along with simultaneous computations of the chemically reacting gas and fiber surface species are shown to provide an enhanced level of understanding of the process. The difficulties in simulating the entire process, as well as the present accomplishments, are discussed, and future directions are suggested.

*NASA Resident Research Associate at Lewis Research Center.

Mission

- Apply existing computational techniques to materials science and develop new ones in order to
  - Understand and improve processes
  - Facilitate design of efficient experiments
  - Develop and test advanced processing concepts with emphasis on optimization
- Provide *easy and informal* access to advanced computational technology in materials science to U.S. industry and universities
- Focus on advanced high-temperature materials for NASA programs such as HiTEMP and the High Speed Civil Transport

CD-91-54150

The Computational Materials Laboratory represents a new venture for the Materials Division at Lewis. Advances in computational sciences and computer hardware have enabled a complementary avenue of research in materials science. The initial efforts in the computational laboratory are concentrated in areas of largest payoffs: space and high-temperature materials processing. The emphasis is on practical and timely solutions to a wide range of real world problems. A relatively unique aspect of the laboratory is the informal and easy access it offers to a variety of organizations that need to develop, understand, or optimize materials processes.

Why Modeling?

Space processing	Earth processing
Few, unique, very expensive experiments	Many, similar, relatively inexpensive experiments
Need better understanding of fundamentals	Cut lead time of new materials development
Very high cost	Very high cost

Modeling can

Enhance level of fundamental understanding, thereby leading to

- Shorter development time
- Cost-effective and timely solutions

CD-91-54151

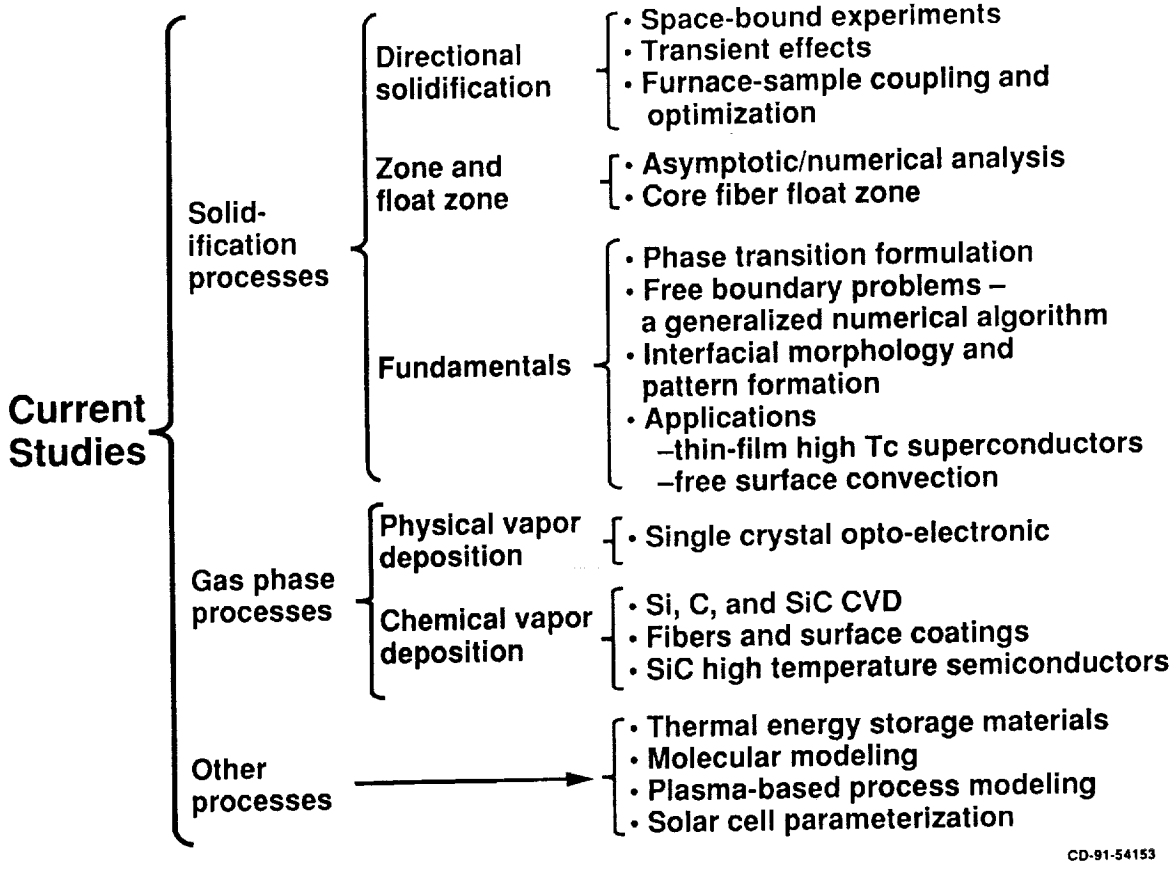
Both space and earth-bound processing require large investments in time and money. Although space experiments are few and unique, they are individually very expensive, and the limited access to space prohibits the usual iterative experimental design. Earth processing involves relatively inexpensive experiments, but the total number needed for the development of new materials or processes usually results in a very long lead time and a large investment. A directed modeling program in tandem with the traditional experimental approach can cut the development time and lead to a greater understanding of the process.

Underlying Physical Phenomena in Materials Processing

	Directional solidification	Chemical vapor deposition
Usage	Ranges from semiconductors to gas turbine blades	Composite fibers, tailored surface coatings, optical fibers
Process parameters	Thermal profile	Thermal profile
Basic phenomena	Heat and mass transport due to density gradients	Heat and mass transport due to density gradients
Unique characteristics	Phase change boundary	Chemical reactions, radiation heat transport
Mathematical description	Navier-Stokes equations	Navier-Stokes equations

CD-91-54152

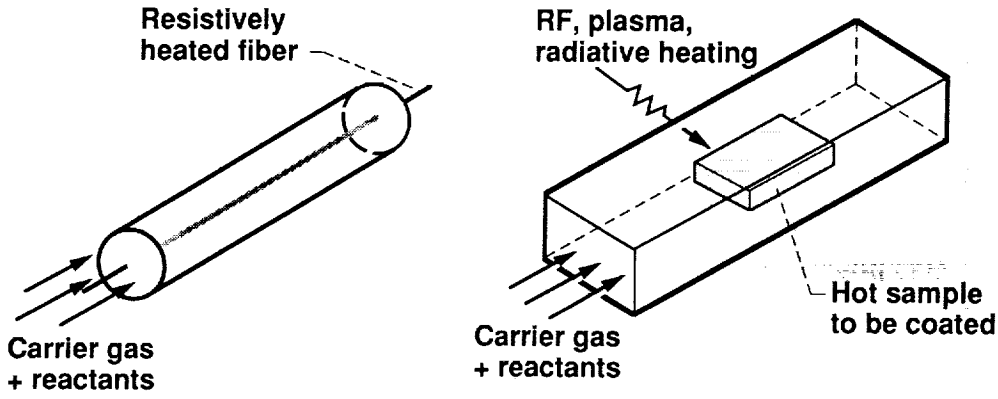
The primary reason for the success of the computational approach is the similarity in the underlying physical phenomena among seemingly different processes. For example, most processes are based on phase transformation from either the gas or liquid states to the solid state; and processes are typically governed by an intricate balance of heat and mass transport, and possible chemical reactions. The mathematical description of transport phenomena from a macroscopic viewpoint is provided by the Navier-Stokes equations. Therefore, fairly generic computational techniques developed elsewhere can be employed in the study of similar processes. Only relatively minor modifications are usually needed then after an initial investment in describing one such process.



The initial emphasis in the Computational Materials Laboratory reflects a heavy investment by the space community, where modeling contributions have already been realized. At this stage we are increasing our effort in the study of high-temperature materials. The chemical vapor deposition (CVD) process is being intensely investigated in a combined experimental/computational study. Future work will be directed at process optimization, and at modeling of processes strongly affected by transport phenomena, both diffusion and convection.

Chemical Vapor Deposition

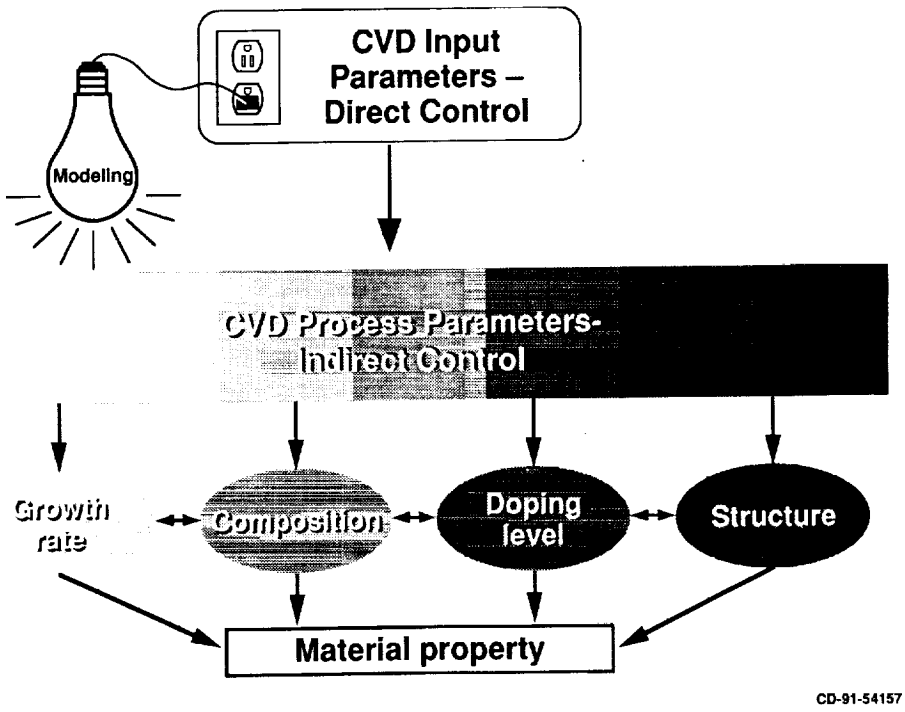
- Versatile technique, easily tailored for
  - Fiber growth and coating
  - Environmental coating and infiltration



- Process involves
  - Transport of heat and mass in the gas stream
  - Simultaneous chemical reactions in gas stream and on the sample surface

CD-91-54156

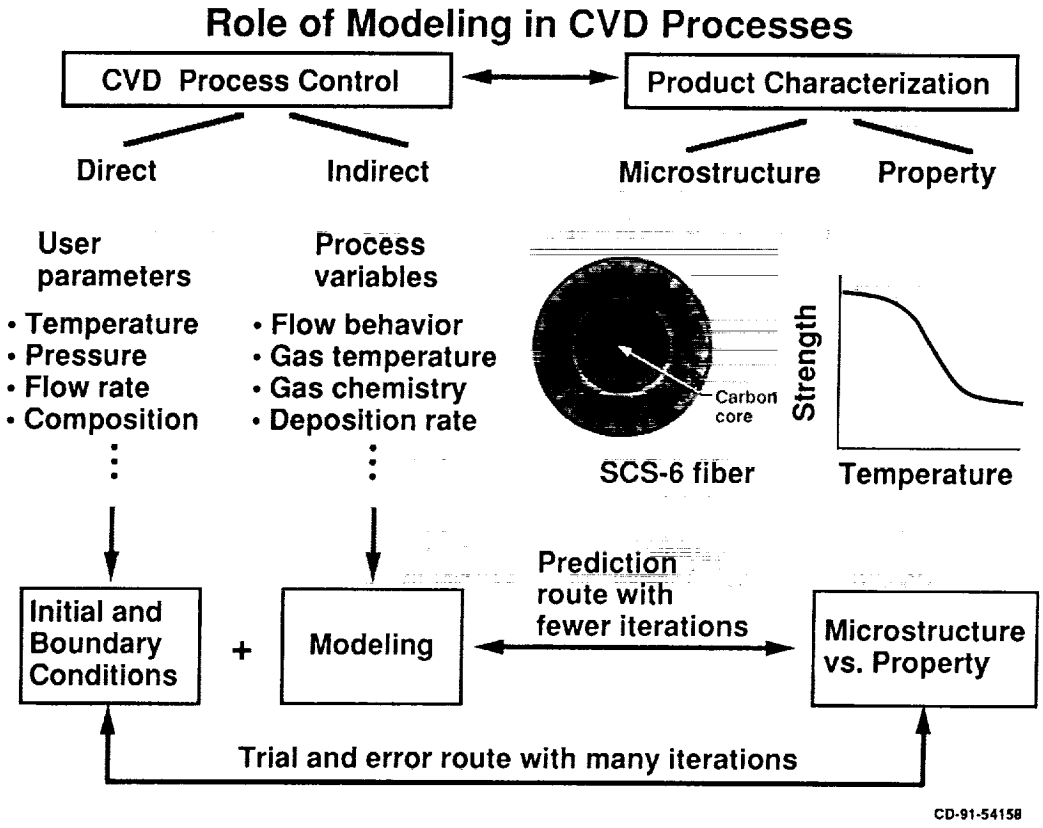
The CVD process is a general purpose, efficient technique for such diverse applications as semiconductor film growth, composite materials fiber growth and coating, and environmental coating including bulk infiltration. In this process a sample heated via RF, joule-heating, or other method is placed in a reactor and exposed to a flow of carrier and chemically reacting gases. Subsequent simultaneous gas and surface reactions result in the growth of a surface layer of a tailored chemical composition and, sometimes, microstructure. Because of its versatility and relative simplicity, the CVD process is growing in popularity. At Lewis it is applied for high temperature semiconductor work (SiC), for fiber production (SiC, other), and for environmental durability coatings.



The CVD process, although simple to describe, comprises a very complex combination of simultaneous phenomena which interact to form a growing structure on the surface. The problem of designing and optimizing the process is common to all processes: How do we alter the process *output* parameters (growth rate, composition, doping, and microstructure) when we have direct control of the *input* parameters only?

This problem can, in principle, be addressed via several approaches, including a "black box" process optimization methodology. Treating the process as a whole, and using statistical and other optimization tools, can provide relatively quick results, but this does not further our understanding of the process. Furthermore, such action does not provide a clear path for process scaleup; a research process that is optimized on the laboratory scale generally cannot be directly translated into a production scale by using process optimization alone. Only a process-motivated fundamental analysis can, in the long run, provide the knowledge required for process alteration or scaling.

The present state of the art in fundamental CVD modeling allows researchers to understand the relations among the process input parameters that lead to certain growth rate characteristics. We also are beginning to correlate those variables with surface composition, but present day models still cannot adequately explain the resulting microstructure. Nevertheless, even prediction and control of growth rates may offer substantial benefits to process designers, and can sometimes be well-correlated with the microstructure.



In analyzing the CVD process, we distinguish among direct and indirect parameters. The former refer to variables which are controlled by the user, whereas the latter are the result of the fluid, heat, and mass transport combined with simultaneous chemical reactions in the reactor. Fundamental process analysis helps explain how the direct parameters result in an indirect process behavior. Such knowledge can result in fewer iterations in the laboratory and a more rapid transfer of a laboratory experiment into a production process.

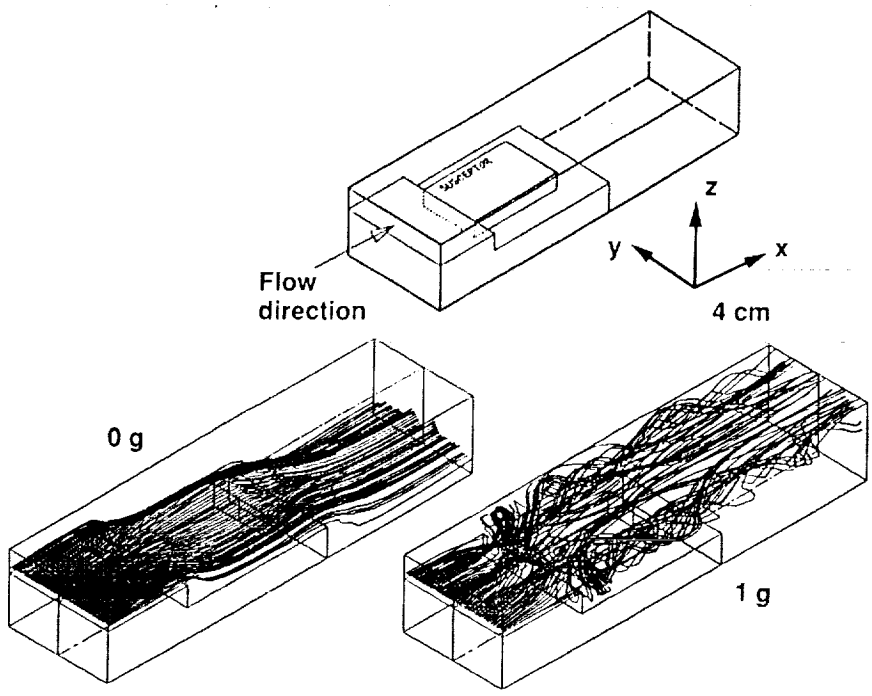
General Characteristics of Lewis CVD Models

- Three-dimensional steady momentum, heat, and mass transport
- Variable properties, including density for nondilute systems
- Secondary transport effects of significance to CVD: Söret diffusion
- Finite rate chemical kinetics in the gas phase
- Finite rate chemical kinetics on the surface, including sticking probabilities

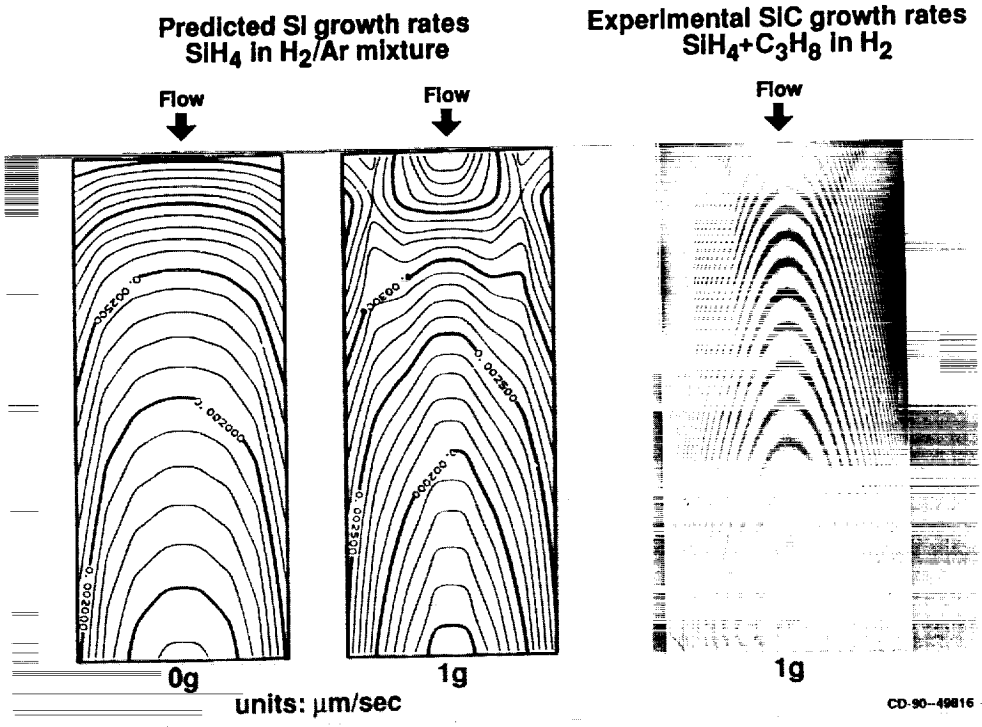
CD-91-54159

The modeling codes for CVD applications at Lewis are based on modified general purpose computational fluid dynamics codes. These codes, which permit arbitrary three-dimensional geometries, solve for the fluid, heat, and mass transport in the reactor, and the simultaneous chemical reactions in the gas and on the surface. The chemistry models include finite rate reactions, allowing for realistic kinetic effects. Other secondary transport mechanisms, such as Soret transport of mass due to thermal gradients (in contrast to the common Fickian diffusion of mass due to concentration gradients), are also included. These second-order effects can become the predominant mechanisms in fiber growth if very steep thermal gradients are present in the vicinity of the fiber surface.

Modeling of Si CVD Coating

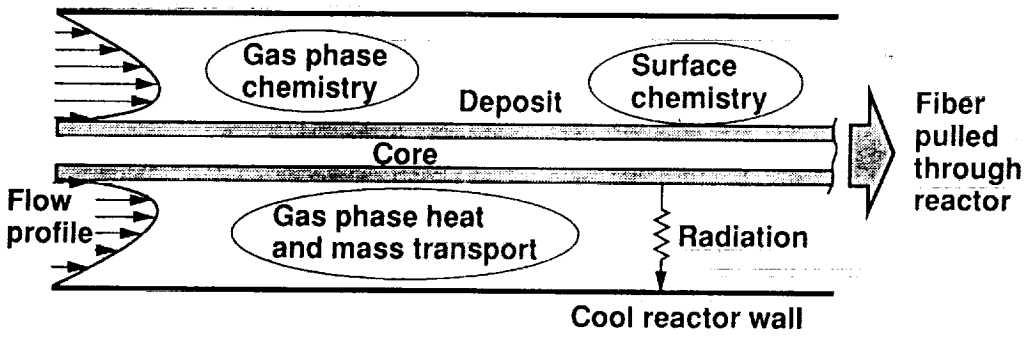


An initial model development and verification study was directed at simulating a well-documented CVD experiment, Si coating of a flat graphite susceptor. The rectangular channel reactor was water cooled, and the sample was heated by an RF field. A complex, three-dimensional flow field resulted from a combination of natural convection originating from the strong density gradients (due to thermal gradients between the hot sample and the cooled walls) and the forced flow of gases through the reactor. Fundamental models allow researchers to explore the origins of transport patterns in the reactor. The simulation shown on the left explores the role of buoyancy driven convection by artificially setting the gravity level to zero, thereby eliminating buoyancy altogether. The flow through the reactor (visualized by following traces of massless particles injected into the reactor) is much more uniform without the corkscrew-like convective rolls that caused complex three-dimensional temperature and chemical species fields, and ultimately, nonuniform surface deposition.



The computed deposition rate contour maps for the previous figure are shown in the left two plots. Both the appearance of the contours and the rates of deposition (in one g) closely correspond to the laboratory measured values. A comparison to the zero-g case (on the left) elucidates the deleterious effects of the corkscrew convection resulting from buoyancy. It is interesting to note that the contour map of the laboratory grown SiC film qualitatively resembles those of the computed patterns, even though the computed chemistry did not consider the carbon species, and the reactor geometry and operating conditions were not identical for both cases. For this particular configuration both of the processes were limited by the transport of chemically reacting species to the surface; therefore, similar growth rate contours resulted.

Fiber CVD

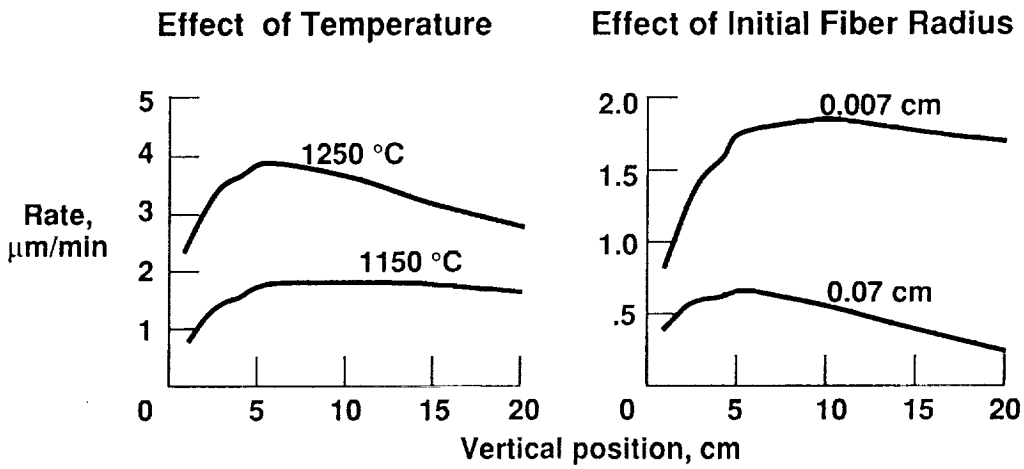


- Gas phase and surface chemistries are practically unknown
- Growth rates vary both axially and radially
- Söret diffusion is much more important than in other conventional CVD reactors
- Radiation effects are significant
- Fiber temperature control is extremely difficult with resistive heating

CD-91-54162

Chemical vapor deposition modeling of SiC or other fiber growth is easier in one respect than the previously shown case, but it is also more complex because of additional nontrivial aspects. Although the cylindrical geometry lends itself to easier model description (axisymmetric versus three-dimensional), the effects of secondary transport modes (Soret) become dominant and require very fine computational meshing near the fiber. Additionally, a common problem for all computational chemistry codes is the lack of reliable chemical kinetics data, especially for exotic Si and C carriers. At present, this last difficulty represents the most important challenge yet to be overcome.

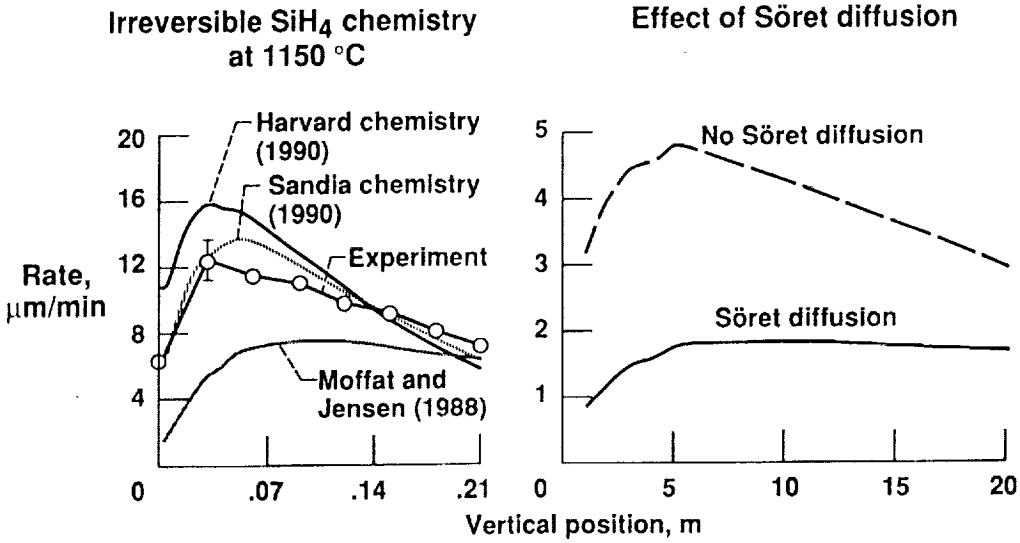
Processing Parameters Effects on Deposition Rates and Uniformity



CD-91-54163

These plots show the level of practical understanding gained from fundamental fiber CVD modeling. The plot on the left shows axial deposition rate distributions (i.e., along the fiber from inlet to outlet) as functions of fiber temperature. The point to be stressed here is that a 100-°C difference in fiber temperature produces a two-fold difference in deposition rate. The more rapid deposition at the elevated temperature causes subsequent depletion of nutrients in the reactor thereby resulting in uniformly decreasing deposition rates along the fiber. The lower temperature setting, although producing lower instantaneous deposition rates, does not deplete the nutrients in the reactor, so very uniform rates are established once the initial transient heating stage is passed. From an operational viewpoint, a 100-°C control of a growing fiber which is resistively heated can be very difficult because of the constantly changing fiber resistivity during the growth. The feedback and process sensitivity to direct parameter settings are clearly understood from this example of results available from fundamental process modeling. Similarly, other "what if" questions can be answered easily with a model. For example, the surface area of a larger initial fiber causes an increase in the deposition rates, as shown on the right plot.

Subtle Effect on Deposition Rates
Need for Fundamental Understanding

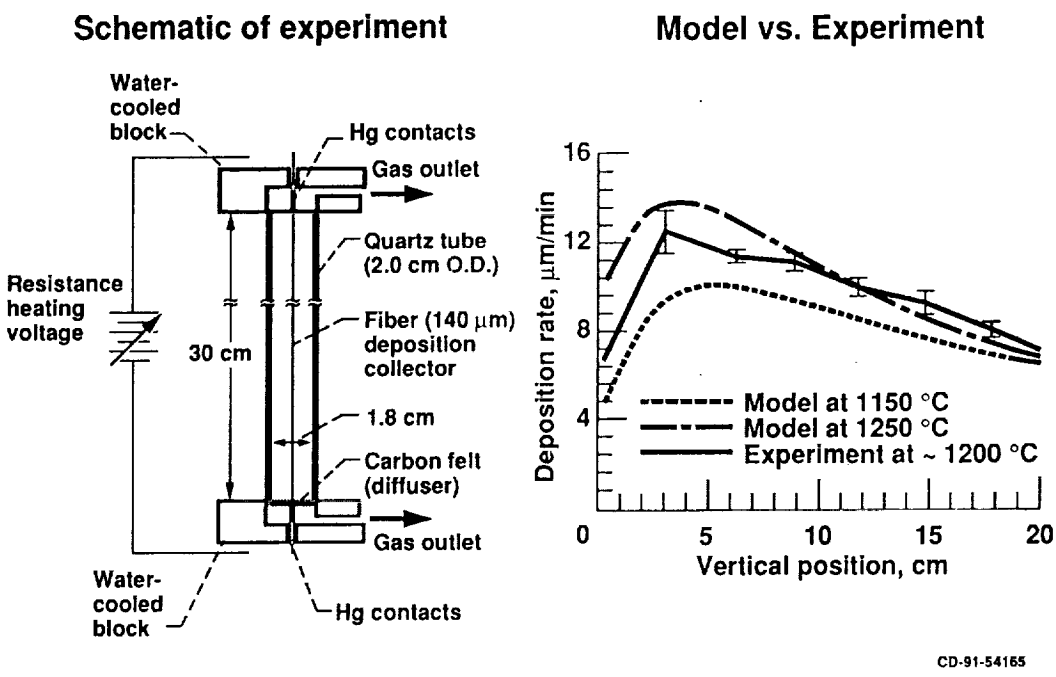


CD-91-54164

The requirements for a successful fundamental process modeling are highlighted in the two plots shown in this figure. The left graph underscores the uncertainties involved in using different chemical kinetics data obtained from recent literature. It is clear that an ad-hoc reliance on published data is unwarranted even for this well-studied system. More complex chemical molecules will result in even more difficult chemistries. Clearly, research in basic computational chemistry and detailed kinetics measurements are needed.

The plot on the right is a rather dramatic example of the effect of Soret diffusion on the process. Soret diffusion is the separation of species of different molecular weights because of steep thermal gradients. This effect is traditionally thought to be of secondary importance for most applications, but in fiber growth, where the radial temperature gradients in the very near vicinity of the fiber might be of the order of 10^4 to 10^5 °C/cm, the Soret effect becomes the dominant mechanism in the transport of species to the fiber and must be included in any viable fiber CVD model.

Comparison of CVD Model Predictions With Experimental Measurements for Si Deposition Rates



An experimental verification of deposition rates along the fiber in a specially built reactor has shown good agreement with modeling results, both qualitatively and quantitatively. Future use of the model is directed at providing guidance for CVD fiber reactor design and operation, with the goal of producing uniform deposition rates.

Conclusions

- Computational materials science is an emerging discipline with a potential for
  - Enhancing our level of understanding of materials processes
  - Accelerating development of new materials
- The Materials Division has established a dedicated Computational Materials Laboratory for simulating advanced materials processing with an emphasis on timely and relevant solutions for processes involving
  - Phase change
  - Transport of and reactions among chemical species
  - Complex fluid, heat, and mass transport
  - Process optimization

CD-91-54166